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PAPER

The oxidative esterification of glycerol to methyl glycerate in methanol using gold on oxidic supports: an insight in product selectivity†

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Gold nanoparticles on different oxidic supports (TiO_2, Al_2O_3 and ZnO) have been studied for the oxidation of glycerol in methanol, using molecular oxygen as the oxidizing agent in a batch set-up. The main oxidation products are methyl glycerate and dimethyl mesoxalate in over 95% selectivity at high glycerol conversion, indicating that C–C bond scission occurs at a significantly lower extent compared to glycerol oxidations in water. The product selectivity is a function of the support. Highest selectivity (82% at 72% conversion) to methyl glycerate is observed in the case of Au/TiO_2 as the catalyst. The use of a base is not essential for the glycerol oxidation reaction to occur, although for TiO_2 and Al_2O_3 higher initial activities are found in the presence of sodium methoxide. Au/ZnO gives comparable activity and selectivity both in the presence and absence of a base. Oxidation experiments with reaction intermediates indicate that oxidation of methyl glycerate to higher oxygenates does not occur to a significant extent in methanol. An alternative pathway for the formation of dimethyl mesoxalate involving dihydroxyacetone is proposed.

1. Introduction

Throughout the last decade, the production of biodiesel *via* the triglyceride transesterification process has increased substantially. Biodiesel production *via* this process is associated with glycerol production (about 0.1 tonne of glycerol per tonne of biodiesel). The European Union is aiming for a 10% substitution of biofuels in the transportation sector by the end of 2020 which requires 17.4 million tonnes of biodiesel production per year and hence may produce 1.74 million tonnes of glycerol as a by-product.[1]

To increase the economic viability of biodiesel production, the development of new glycerol outlets in the form of value added products is of high importance. A large number of glycerol related publications and reviews on potential high value components from glycerol have appeared over the last five years.[2–6]

Oxidation of glycerol in water using supported noble monometallic (Au or Pt) or bimetallic (Au–Pt or Au–Pd) catalysts in the presence of a base, aiming at glyceric acid as the desired product has been intensively explored by various research groups.[7–11]

Glyceric acid is an interesting tri-functional molecule, present as a metabolite in the glycolysis cycle and a precursor in the synthesis of serine.[12] It also serves as a food supplement, anti-cirrhosis agent and chelating agent.[13]

Most of the catalytic studies on glycerol oxidation refer to Au nanoparticles supported on carbon. Carrettin *et al.* have reported 100% selectivity to glyceric acid at 56% conversion in the presence of stoichiometric amounts of sodium hydroxide.[14] Only a limited number of studies have been reported on the use of Au catalysts on supports other than carbon in the aqueous phase oxidation of glycerol. Gold nanoparticles on metal oxide supports have been proven to be less active for aqueous phase glycerol oxidation compared to carbon supported catalysts.[15,16]

The activity and selectivity of the Au catalysed glycerol oxidations in water depends on the particle size of the gold nanoparticles and the pH of the reaction medium. The presence of a base is required for the abstraction of a proton from glycerol to form a glycerolate anion.[17] Generally, with a high concentration of NaOH, a high glycerol conversion and glyceric acid selectivity is observed.[14]

The selectivity of the oxidation reactions is a major concern. Numerous oxygenates such as glyceraldehyde (GLA), dihydroxyacetone (DHA), glyceric acid (GLYA), tartronic acid (TART), mesoxalic acid (MOXA), glycolic acid (GLYC), formic acid (FORM), oxalic acid (OXAL) and lactic acid (LACT) may be formed, see Scheme 1 for details.[10,18]

The formation of C_2 compounds is indicative of C–C bond scission. This scission process is likely the result of the action of *in situ* formed hydrogen peroxide.[19]

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Solvent effects on the oxidation of glycerol with supported Au catalysts have not been studied in detail and to date, only one article describing the oxidation of glycerol in methanolic solution has been published by Taarning *et al.* Here, the oxidation of glycerol at 373 K in methanol in the presence of 10 mol% sodium methoxide using Au catalysts on inorganic supports (TiO_2 and Fe_2O_3) was reported to give dimethyl mesoxalate as the major product in selectivities up to 89 and 79% over Au/Fe_2O_3 and Au/TiO_2, respectively.[20] The selectivity to methyl glycerate was always less than 20%. Since the waste stream from biodiesel production contains a mixture of glycerol and methanol, methanolic oxidation is an attractive methodology.[21]

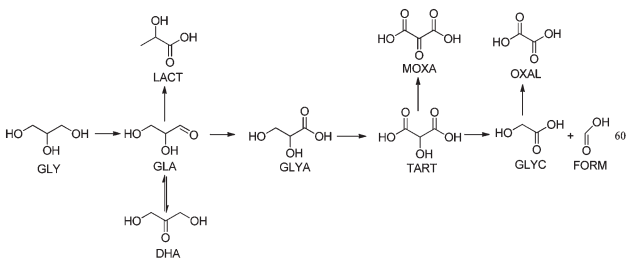
When oxidising glycerol in methanolic solution, the oxidation of methanol is a concern. Hayashi *et al*., however, have shown that when oxidizing ethylene glycol using supported gold catalysts in methanol, methanol is hardly converted due to strong adsorption of the ethylene glycol to the catalyst, preventing considerable methanol oxidation.[22]

Here we report our experimental studies on the oxidation of glycerol to methyl glycerate in methanol using Au catalysts on different oxidic supports. Support effects and the role of a base on the activity and selectivity to methylglycerate have been studied and will be reported. In addition, compared to previous publications, an alternative reaction pathway explaining the formation of the product portfolio is proposed.

2. Experimental section

2.1. Materials

Au/TiO_2 (1.2 wt%), Au/Al_2O_3 (0.9 wt%) and Au/ZnO (1.0 wt%), all with Au particle dimensions between 2 and 3 nm, were supplied by Strem-Autek. A deposition/precipitation method was employed for the preparation. Glycerol (≥99%), methanol (anhydrous, 99.8%), sodium methoxide (25 wt% in methanol), methyl glycolate, methyl pyruvate and dimethyl oxalate were obtained from Sigma-Aldrich. Methyl glycerate was procured from Bepharm Ltd Shanghai, China. Dimethyl tartronate (≥ 99% purity by GC) was prepared from tartronic acid (Sigma Aldrich) by refluxing in methanol over Amberlyst 15 (Alfa Aesar) for 24 h. Dimethyl mesoxalate (≥99% purity by GC) was prepared by refluxing diethyl mesoxalate (Sigma Aldrich) in methanol in the presence of sodium methoxide for 24 h. Oxygen (99.995%) was obtained from Linde Gas Benelux B.V., The Netherlands. Glycerol and all the catalysts used in this study were dried before use under vacuum (0.5–2.0 mbar) at 313 K in the presence of phosphorus pentoxide (Sigma Aldrich) for at least 20 h.



Scheme 1 General proposed reaction scheme for aqueous phase oxidation of glycerol in alkaline conditions over Au catalysts.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) measurements were performed with a JEOL JEM 1011 instrument operating at 100 kV. Catalyst samples were finely powdered and dispersed in ethanol. A small drop of this dispersion was deposited on a copper grid coated with carbon. Particle size distributions of the catalysts were determined from the transmission electron micrographs by measuring the dimensions of 150–200 particles. The gold particles were identified using energy dispersive X-ray spectroscopy (EDAX).

ICP-OES analyses to determine the amount of metals in the solid catalysts were performed using a Perkin Elmer optima 7000 DV instrument. Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2420 analyser at 77 K. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the surface areas. The pore volume was obtained at a relative pressure of 0.98 in the desorption branch (Table 1).

2.3. Catalyst testing

Oxidation experiments were performed in 75 ml steel autoclaves (Parr Series 5000 Multiple Reactor System). The autoclave was charged with a glycerol solution in methanol (20 mL of a 0.25 molar solution). Subsequently, the catalyst (0.032 mmol Au, 0.52 g for Au/TiO_2, 0.70 g for Au/Al_2O_3 and 0.63 g for Au/ZnO) was added and the autoclave was sealed, flushed and finally pressurized with oxygen to 5 bar. The reactor contents were heated to 353 K under stirring with a magnetic stirring bar (800 rpm). Samples were withdrawn periodically after cooling the reactor to room temperature. Then the reactor was recharged with fresh oxygen to 5 bar and reheated to 353 K. A typical reaction time was 25 h, samples were taken every 5 h.

2.4. Product analysis

Liquid phase samples were analysed by GC (HP equipped with a flame ionization detector and a CHROMPACK capillary column of dimension 25 m × 0.32 mm × 0.30 μm) and GC-MS (InterscienceTraceGC Ultra GC with a Restek GC column Rxi-5 ms

Table 1 Relevant catalyst properties

Catalyst	Au loading (wt%)	Au particle size (nm)	BET surface area ($m^2\ g^{-1}$)	Pore volume (PV) ($cm^3\ g^{-1}$)	Average pore size (nm)
Au/TiO_2	1.2	2–3	50.1 ± 0.3	0.352	28.1
Au/Al_2O_3	0.9	2–3	224.9 ± 0.4	0.612	10.9
Au/ZnO	1.0	2–3	45.3 ± 0.1	0.249	22.0

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30 m × 0.25 mm × 0.25 μm connected to a Interscience Trace-DSQ II XL quadrupole mass selective detector (EI, mass range 35–500 Dalton, 150 ms sample speed).

For GC analysis the injector and detector temperature were set at 250 and 280 °C, respectively. Helium was used as the carrier gas with a flow rate of 50 ml min^{-1}. A split ratio of 1 : 25 was applied. Peak identification for methyl glycerate, dimethyl tartronate, dimethyl mesoxalate, methyl pyruvate, methyl glycolate, and dimethyl oxalate was confirmed by injection of reference compounds. Quantification was done on the basis of response factors which were determined for each component by injecting known concentrations.

HPLC was used to identify and quantify glyceraldehyde and dihydroxyacetone. Analyses were performed on a Waters HPLC instrument equipped with a Shodex-Ionpak KC-811 (30 cm length) column maintained at 85 °C using H_2SO_4 (3 mM) in ultra-pure water as the eluent with a flow rate of 1 ml min^{-1}. The components were identified using a UV (210 nm) and an RI detector. The concentrations in the samples were determined using calibration curves obtained by injecting standard solutions of known concentrations of glyceraldehyde and dihydroxyacetone.

3. Definitions

Glycerol conversion is defined as:

$$X_g = \frac{C_{g,0} - C_g}{C_{g,0}} \quad (1)$$

where C_g is the concentration of glycerol after a certain reaction time and $C_{g,0}$ is the initial glycerol concentration.

Product selectivity for a compound P is defined as

$$S_p = \frac{C_p}{C_{g,0} - C_g} \quad (2)$$

where C_p is the concentration of a product after a certain reaction time.

Mass balance closure was calculated on the basis of all products quantified by GC and HPLC analyses.

4. Results and discussion

The oxidation reactions of glycerol in methanol were typically carried out at 353 K using molecular oxygen (5 bar) as the oxidant. A variety of Au catalysts on different supports (TiO_2, Al_2O_3 and ZnO) were explored. An overview of the results of the experiments is given in Tables 2 and 3. The presence of Au nanoparticles is essential, and separate reactions with the individual supports (no Au present) did not lead to any appreciable glycerol conversion. In addition, no reactions were observed in the absence of any catalysts, an indication that homogeneous reactions by small amounts of metals in the starting materials or from the reactor wall do not occur at the prevailing conditions.

Carbon balances were determined for all experiments and good closures (>95%) were obtained. Reproducibility was tested by performing duplicate experiments at similar conditions and intakes. Good agreements for conversion and product selectivity were observed (less than 5% deviation).

4.1. Oxidation of glycerol in methanol using supported Au catalysts in the presence of base

The results for catalytic glycerol oxidations using the Au on different oxidic supports in the presence of a catalytic amount (10 mol%) of base are summarised in Table 2. Glycerol (GLY) oxidation over Au/TiO_2 led to 48% glycerol conversion after 5 h. The main product was methyl glycerate (MGLY), with a selectivity of 72%. By-products were dimethyl mesoxalate (DMM, 7% selectivity) and glyceraldehyde/dihydroxyacetone

Table 2 Oxidative esterification of glycerol over Au catalysts in the presence of 10 mol% NaOMe on glycerol[a]

Catalyst	Time (h)	Glycerol conversion (%)	Selectivity (%)						Carbon mass balance closure (%)
			GLA/DHA	MGLY	DMT	DMM	MPYR	MGLYC	
Au/TiO_2	5.0	48	9.0	72.0	2.0	7.0	2.0	2.0	95.0
Au/TiO_2	30	72	1.0	82.0	1.0	9.5	1.0	0.5	95.0
Au/Al_2O_3	5.0	78	1.5	36.5	1.5	57.0	n.d.	1.5	98.0
Au/ZnO	5.0	76	18	43.0	1.0	33.0	n.d.	1.0	97.0

[a] T = 353 K, P (O_2) = 5 bar, molar ratio glycerol to methanol is 1 : 99, molar ratio glycerol to Au is 153, n.d. = not detected.

Table 3 Oxidative esterification of glycerol over Au catalysts in base free conditions[a]

Catalyst	Time (h)	Glycerol conversion (%)	Selectivity (%)						Carbon mass balance closure (%)
			GLA/DHA	MGLY	DMT	DMM	MPYR	MGLYC	
Au/TiO_2	5.0	24	12.5	52.0	2.0	15.0	15.5	2.0	99.0
Au/TiO_2	25	90	1.0	50.0	1.0	31.0	11.0	3.0	97.0
Au/Al_2O_3	5.0	56	6.5	30.5	1.0	59.0	2.0	1.0	100
Au/Al_2O_3	10	66	2.0	32.5	0.8	62.0	1.5	1.0	99.8
Au/ZnO	5.0	71	21.0	34.5	1.8	40.0	0.94	1.0	99.0

[a] T = 353 K, P (O_2) = 5 bar, molar ratio glycerol to methanol is 1 : 99, molar ratio glycerol to Au is 153.

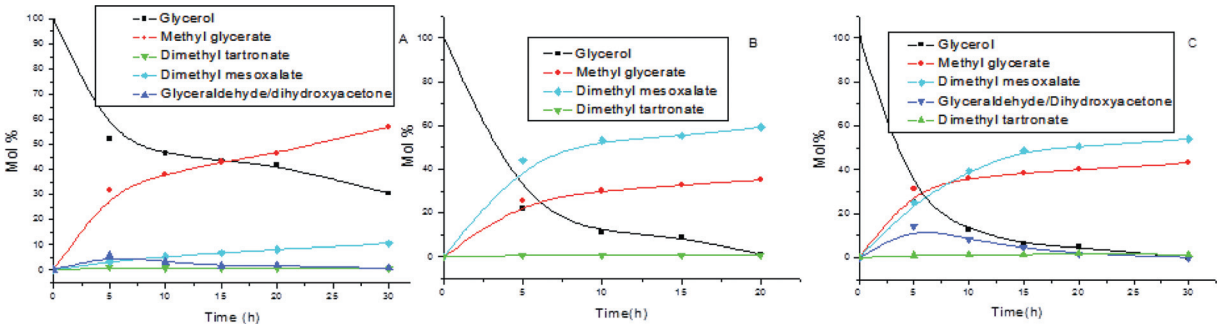

Fig. 1 Oxidative esterification of glycerol in the presence of 10 mol% base (NaOMe) over (A) Au/TiO_2, (B) Au/Al_2O_3 and (C) Au/ZnO.

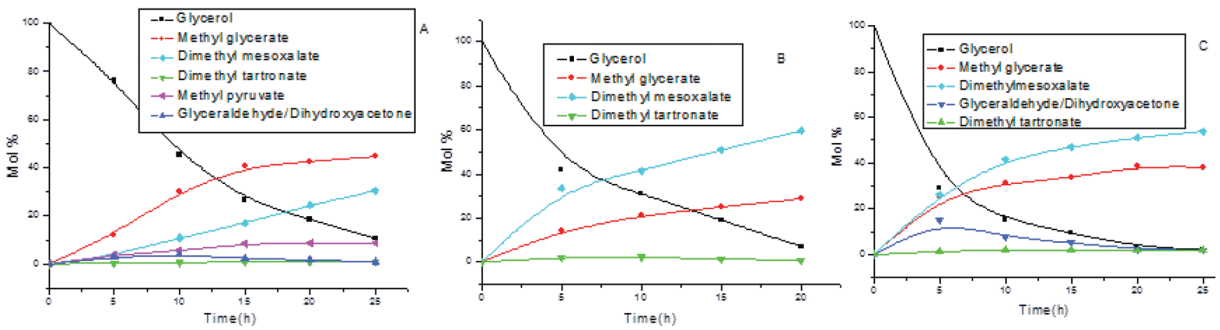

Fig. 2 Oxidative esterification of glycerol in base free conditions over (A) Au/TiO_2, (B) Au/Al_2O_3 and (C) Au/ZnO.

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(GLA/DHA, 9% selectivity). The sum of the GLA and DHA concentration is reported as the GC technique used does not allow the quantification of the individual components. Small quantities of methyl pyruvate (MPYR, 2%), methyl glycolate (MGLYC, 2%), dimethyl oxalate (1%, DMO) and dimethyl tartronate (DMT, 1–2%) were also observed. At extended reaction times (30 h), the glycerol conversion increased to 72%. A MGLY selectivity of 82% and a DMM selectivity of 9.5% were obtained at this glycerol conversion level (Fig. 1A).

When the oxidation was performed using Au/Al_2O_3 as the catalyst, the glycerol oxidation rate was higher and 78% glycerol conversion was achieved in 5 h (Fig. 1B). Longer reaction times (10 h) gave 89% conversion. These conversions are considerably higher than when using the TiO_2 support. The main products after 5 h are again the C_3 components MGLY (36.5% selectivity) and DMM (57% selectivity), though the selectivity is reversed compared to the data for the TiO_2 support. Small quantities of DMT and MGLYC (1.5% each) were also observed (Table 2).

When using Au/ZnO as the catalyst, the activity is similar to that of Au/Al_2O_3 and 76% glycerol conversion was observed after 5 h reaction time (Fig. 1C). A further extension to 10 h resulted in 85% glycerol conversion. However, the selectivity to MGLY is considerably lower than in the case of TiO_2, and, as with alumina, significant amounts of DMM were formed. For this catalyst, the selectivity to GLA/DHA is much higher (18% after 5 h) than for the other catalysts. Products such as DMT, MGLYC and DMO were observed in small quantities (all together 3%).

Thus, when aiming for a high chemoselectivity of MGLY, Au on TiO_2 is the preferred catalyst, though the activity is the lowest of the three catalysts tested.

4.2. Oxidation of glycerol in methanol using supported Au catalysts at base free conditions

Until recently, it was generally assumed that the first step of the Au catalysed oxidation of glycerol involves deprotonation of glycerol by a base to yield a glycerolate anion. However, recent studies have indicated that glycerol is oxidised to glyceric acid using Au on acidic or basic supports in aqueous conditions even in the absence of a base, indicating that a base is not always necessary.[23,24] We therefore decided to investigate the Au catalysed oxidation of glycerol in methanol also in the absence of a base and the results are summarised in Table 3.

An oxidation reaction performed using Au/TiO_2 at 353 K and 5 bar oxygen pressure, gave 24% glycerol conversion after 5 h with MGLY (52%) as the main oxidation product. Significant amounts of GLA/DHA (12.5%), DMM (15%) and MPYR (15.5%) were also observed. Prolonged reaction times (25 h) led to 90% glycerol conversion. At this conversion MGLY is still the main product (50% selectivity), though, in particular, the amount of DMM (31%) has increased considerably, at the expense of GLY/DHA.

The glycerol conversion *versus* time profile for the reaction in the presence and absence of base differs considerably (Fig. 1A *vs.* Fig. 2A). In the presence of a base, the initial reaction rate is higher, though the conversion at prolonged times is lower. This is indicative for a catalyst deactivation pathway in the presence of a base. This deactivation pathway is suppressed in base free conditions (*vide infra*). Regarding MGLY selectivity, the desired product in this study, it appears beneficial to work in the presence of a base (60% yield in the presence of base *versus* 45% yield in base free conditions after 25–30 h).

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When the glycerol oxidation was conducted under base free conditions using Au/Al_2O_3 as the catalyst, 56% glycerol conversion was obtained after 5 h and this increased to 66% after 10 h. The major product is DMM, in 59–64% selectivity.

The selectivity for MGLY is lower and is between 30.5–32.5%. The yield of both MGLY and DMM increases as the reaction proceeds, without significant change in the overall selectivity pattern (Fig. 2B). The presence of base has a significant influence on the activity when using Au/Al_2O_3 as the catalyst whereas MGLY selectivity was enhanced only up to 4–5%.

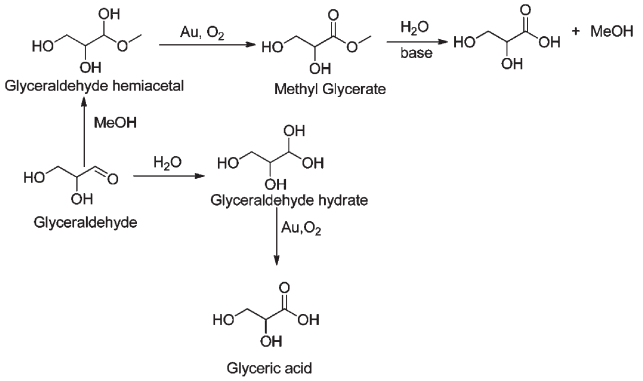
When Au/ZnO was used as the catalyst in base free conditions, conversion reached 71% after 5 h and 91% after 15 h. The main product is DMM (40–42%), whereas also considerable amounts of MGLY (34.5–36%) and GLY/DHA (21%) were obtained (Fig. 2C). The effect of base on glycerol conversion while using Au/ZnO is relatively small whereas the selectivity towards MGLY was enhanced to 43% in the presence of base.

4.3. Catalyst activity and stability

All three Au catalysts on oxidic supports were active under base free conditions, implying that a base is not essential for the oxidation of glycerol over Au catalysts in methanol. However, the initial activities of the catalysts are higher in the presence of a base when using the TiO_2 and Al_2O_3 supported Au catalysts. The difference in activity in the presence and absence of a base is much less for the Au/ZnO catalyst (Tables 2 and 3).

For the Au/TiO_2 catalyst, a decline in catalytic activity after 5 h was observed in the presence of a base, indicative for catalyst deactivation (Fig. 1A). Characterization of the catalyst after reaction with TEM and ICP-OES shows that both sintering of Au clusters and Au leaching to the liquid phase did not occur to a significant extent. In addition, the BET area of the catalyst before and after the reaction is essentially similar. A possible deactivation mechanism in the presence of considerable amounts of free glycerate in the mixture when performing the reactions in the presence of a base is discussed below. Recently Worz *et al.* reported that glycerate acts as a strong chelating agent for noble metals and suppresses glycerol conversion to a large extent.[25] Adsorption of α-hydroxy acids in a bidentate mode on oxidic supports such as TiO_2 and Al_2O_3 has also been reported in the literature.[26,27] Small amounts of glycerate may be formed by the alkaline catalysed hydrolysis of the ester product or by a hydrate route (Scheme 2). The required water for these reactions may be formed by decomposition of hydrogen peroxide, a known reactive intermediate in the reaction sequence.[19,20]

Catalyst deactivation is less pronounced for Au/Al_2O_3 and Au/ZnO compared to Au/TiO_2 (Fig. 1), indicating that glycerate inhibition is less pronounced for the former catalysts. To gain insights in to these differences, IR spectra of the spent catalyst were recorded. For Au/TiO_2, clear adsorption bands corresponding to glycerate adsorption were observed in the range 1610–1661 cm^{-1} for CO_2^- stretching vibrations. These bands appear at 1587–1636 cm^{-1} for aqueous glycerate. The increase in the wavenumbers indicates the formation of metal carboxylates. The bands at 1119 and 1113 cm^{-1} can be assigned to the C–O stretch of the adsorbed α-hydroxy group of glycerate. This band appears at 1112 cm^{-1} for aqueous glycerate (see ESI† for IR-spectra and experimental procedure). These characteristic adsorptions are less pronounced for the other two catalysts. It thus appears that glycerate adsorption leading to catalyst deactivation occurs at a larger extent for Au/TiO_2 than for Au/Al_2O_3 and Au/ZnO.



Scheme 2 Possible pathways for the formation of glycerate.

Besides MGLY, DMM is also present in significant amounts in the reaction mixture (Tables 2 and 3) and as such, the corresponding mesoxalate may also be involved in adsorption processes affecting catalyst activity and selectivity. The IR spectrum of aqueous mesoxalate was recorded (ESI†) and compared to the IR spectra of spent catalysts. Based on the IR data, the presence of a coordinated mesoxalate cannot be excluded *a priori*, though is less likely due to the absence of an α-hydroxy group in mesoxalic acid, which is known to be essential for strong coordination to the support.

Further evidence for glycerate adsorption to the TiO_2 support was obtained by performing a glycerol oxidation experiment with Au/TiO_2 with a known amount of glyceric acid (0.5 mol mol^{-1} Au) present at the start of the reaction. Glycerol conversion was 57% after 20 h in the presence of glycerate whereas 81% conversion was obtained when glycerate was not added under similar conditions. This fact combined with glycerate adsorption on the catalyst surface of spent Au/TiO_2 (IR) is a strong indication that catalyst deactivation is due to glycerate adsorption.

Further evidence that glycerate adsorption is reversible was obtained by performing catalyst recycle experiments with the Au/TiO_2 catalyst. For this purpose, the catalyst used for the oxidation in the presence of a base (after 30 h) was taken and subjected to extraction in a mixture of methanol and water (see ESI† for more details). The catalyst was recovered by filtration, thoroughly washed with methanol and water and dried in a vacuum oven at 313 K in the presence of a desiccant for at least for 20 h. This catalyst was used for a second catalytic glycerol oxidation experiment in the presence of a base. Both the activity profiles as well as the product compositions were similar as for the first experiment, indicating that catalyst deactivation is not caused by an irreversible deactivation process.

4.4 Reaction pathways

The selectivity patterns for glycerol oxidation differ in the presence and absence of base. The selectivity for MGLY is higher in

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the presence of a base for all three catalysts. For glycerol oxidations over Au catalysts in aqueous media, glyceric acid is assumed to be further oxidised to tartronic acid, and subsequently to mesoxalic acid[10,28] (Scheme 1). When a similar sequence is operative in methanol, this would imply that initially formed MGLY is converted to DMT which is subsequently oxidised to DMM. This sequence was also suggested by Taarning *et al.* for the Au catalysed glycerol oxidations in methanol.[20]

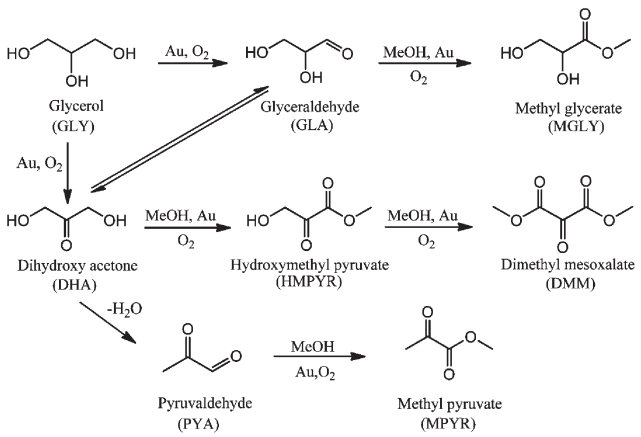
To gain more insights into the reaction pathways for the oxidation of glycerol with supported Au catalysts in methanol, a number of catalytic oxidation experiments were performed using MGLY as the starting compound. Both in the presence and absence of a base, the conversion of MGLY was less than 5% at reaction times exceeding 25 h. Product analyses indicated the formation of small amounts of DMT (1–3%), while the amount of DMM was negligible. However, in the catalytic oxidations using glycerol, DMM formation was significant under these conditions; see Tables 2 and 3 for details. These results strongly indicate that MGLY is likely not the precursor for DMM formation and that an alternative reaction pathways for the production of DMM is operative.

Further information comes from glycerol oxidation experiments using the Au/TiO_2 catalyst in the absence of base. Here, a significant amount (11–15.5%) of methyl pyruvate (MPYR) was observed. The formation of both MPYR and DMM may be explained by the involvement of dihydroxyacetone (DHA) in the reaction mechanism (Scheme 3). To prove this, the oxidation of DHA in base free conditions was performed using the three Au catalysts, see Table 4 for details.

For all reactions, about 87–90% conversion of DHA was observed in 5 h reaction time and the main product was DMM (>55%). Using the Au/TiO_2 catalyst, significant amounts of MPYR were formed (17%) as well. The formation of the latter likely involves pyruvaldehyde (PYA) as the intermediate. PYA was indeed detected (GC-MS) in minor amounts. The conversion of trioses like DHA to pyruvaldehyde is known to be catalysed by Lewis acid centers.[29]

These results clearly indicate the involvement of DHA in the reaction network. To assess whether DHA is indeed formed in the catalytic glycerol oxidation experiments, the reaction mixtures were analysed by HPLC. This technique allows the detection and quantification of DHA in the presence of GLA, which is not possible with the standard GC technique used in this study. The results of these analyses are provided in Table 5. For all catalysts, DHA was present in the reaction mixture in amounts between 2 and 27 mol%.

Based upon this information, an alternative reaction scheme differing from those previously published, is proposed for the oxidation of glycerol in methanol over Au catalysts (Scheme 3). Two main pathways are operative, (i) the oxidation of GLA to MGLY and (ii) a pathway involving DHA leading to the formation of DMM and MPYR. DHA and GLA are known to interconvert under basic aqueous conditions.[30,31] The relative rates of both pathways are determined by (i) the reaction rates of GLA to MGLY, (ii) DHA to HMPYR and (iii) the rate of DHA–GLA interconversion. Proper kinetic modelling will be required to assess which of the steps is rapid at the conditions employed and determines product selectivity.



Scheme 3 Proposed reaction pathway for the oxidative esterification of glycerol over Au catalysts in methanol.

Table 4 Oxidative esterification of DHA in base free conditions[a]

Catalyst	Conv. (%)	Selectivity (%) GLA	MGLY	MPYR	DMT	HMPYR	DMM
Au/TiO_2	88	2	14	17	1	6	55
Au/Al_2O_3	90	2	10	3	1.5	5	75
Au/ZnO	87	5	13	<1	1.5	5	70

[a] T = 353 K, P (O_2) = 5 bar, molar ratio glycerol to methanol is 1 : 99, molar ratio glycerol to Au is 153, reaction time = 5 h.

Table 5 Oxidative esterification of glycerol over Au catalysts in base free conditions[a]

Catalyst	Time (h)	Conv. (%)	Selectivity (%) DHA	GLA	MGLY	DMM
Au/TiO_2	5	24	2	10.5	52	15
Au/Al_2O_3	2	32	6	3.0	35	46
Au/ZnO	2	47	27	19.0	31	20

[a] T = 353 K, P (O_2) = 5 bar, molar ratio glycerol to methanol is 1 : 99, molar ratio glycerol to Au is 153.

4.5 Support effects

Reactions over supported gold catalysts have been reported in the literature to be support-structure sensitive.[32] Clear support effects are also observed for the three supports tested in this study, with the Au on titania catalyst showing pronounced different activity and chemo-selectivity profiles. The Au on titania support is the least active catalyst for glycerol oxidation, both in the presence and absence of a base (Tables 2 and 3). Experimental evidence (*vide supra*) indicates that this is due to relative strong adsorption of glycerate to the titania support, and likely involves the Lewis acidic Ti center. The product distribution for the Au on titania catalyst also shows distinct differences compared to the other two catalysts. The MGLY pathway (Scheme 3) is more pronounced than the DMM pathway, whereas also the

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formation of MPYR is considerably higher than for the other catalysts (particularly at base free conditions, Table 3). The latter reaction is known to be catalysed by Lewis acids, another indication that Au/TiO_2 is special due to the involvement of the Ti centers of the support.

5. Conclusions

We have shown that it is possible to convert glycerol in methanol into C_3 methyl esters in high yields without the requirement of a base. The selectivity of the methyl esters is a clear function of the catalyst. The highest selectivity for methyl glycerate (82% at 72% conversion) was obtained using Au/TiO_2. The presence of a base has a positive effect on the initial reaction rate for glycerol and the conversion of glyceraldehyde to methyl glycerate. A novel reaction pathway is proposed on the basis of a thorough analysis of reaction intermediates and products and subsequent catalytic oxidation experiments with these intermediates. At this stage, it has not proved possible to relate catalyst performance and, in particular, support effect with the proposed mechanistic scheme. The reaction network is complex and involves a number of parallel and serial reactions including an equilibrium reaction (GLY to DHA). Detailed kinetic studies are required for all catalysts to unequivocally establish the effects of the catalyst on the individual steps in the reaction network and are scheduled for follow up investigations.

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